PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : B01J 13/14, A01N 25/28 — A1

(11) International Publication Number: **WO 90/11129**

(43) International Publication Date: 4 October 1990 (04.10.90)

(21) International Application Number: PCT/HU90/00021

(22) International Filing Date: 23 March 1990 (23.03.90)

(30) Priority data:
1516/89 24 March 1989 (24.03.89) HU

(71) Applicants *(for all designated States except US)*: NEHÉZVEGYIPARI KUTATÓ INTÉZET [HU/HU]; Wartha V. u. 1, H-8200 Veszprém (HU). MAGYAR VISZKÓZAGYÁR [HU/HU]; H-2537 Nyergesujfalu (HU).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)* : BAGI, Albert [HU/HU]; Május 1 tér 6, H-2537 Nyergesujfalu (HU). FARAGÓ, Jenő [HU/HU]; Esze Tamás u. 3, H-2537 Nyergesujfalu (HU). MEISZEL, László [HU/HU]; Attila u. 22, H-Budapest (HU). HASZNOS, Magdolna [HU/HU]; Stromfeld Aurél u. 5/c, H-8200 Veszprém (HU). PERNYESZI, József [HU/HU]; Klapka Gy. u. 1/A, H-8200 Veszprém (HU). MOGYORÓSY, György [HU/HU]; Celsőzöldmáli út 61-65, H-1025 Budapest (HU). SÁGI, Károly [HU/HU]; Csolnoky u. 5/G, H-8200 Veszprém (HU). SZABÓ, László [HU/HU]; Szabadság tér 8, H-8200 Veszprém (HU). MIKLÓS, Dezső [HU/HU]; Szilfa u. 18, H-8200 Veszprém (HU). SIMON, Katalin [HU/HU]; Egry J. u. 1/E, H-8200 Veszprém (HU). BAGI, László [HU/HU]; Damjanich u. 1/B, H-8200 Veszprém (HU). GESZTELYI NAGY, Judit [HU/HU]; Egry J. u. 18/4, H-8200 Veszprém (HU).

(74) Agent: DANUBIA; P.O. Box 198, H-1368 Budapest 5 (HU).

(81) Designated States: AT, AT (European patent), BE (European patent), BG, CH, CH (European patent), DE, DE (European patent), DK (European patent), ES, ES (European patent), FR (European patent), GB, GB (European patent), IT (European patent), JP, LU (European patent), NL, NL (European patent), RO, SE (European patent), SU, US.

Published
With international search report.

(54) Title: METHOD FOR PRODUCING ECOLOGIC CAPSULE OF NATURAL ORIGIN FOR PRODUCTS WITH CONTROLLED RELEASE OF THE ACTIVE INGREDIENT

(57) Abstract

The invention relates to a process for producing capsule or microcapsule containing cellulose and/or starch. The process according to the invention can be characterized in that 0-50 % by weight of polymers are added to the capsule material of natural origin at a temperature of 10 to 50°C, the suspension is vigorously stirred, thereafter 0 to 50 % by weight of urea-formaldehyde resin pre-condensate are admixed, the colloidal solution thus obtained is applied onto the acid mixture - preferably with 10 % by weight of sulphur acid - containing 0.1 to 5 % by weight of cross-linking catalyst, expediently ammonium sulfate, furtheron 0.01 to 5 % by weight of ethoxylated amine surface-active material, the capsules thus obtained are washed and dried at 40 to 100°C, thereafter different active ingredients respectively the solutions thereof are contacted with the capsule, at last the blotted capsule is to be powdered.

+ See back of page

DESIGNATIONS OF "DE"

Until further notice, any designation of "DE" in any international application whose international filing date is prior to October 3, 1990, shall have effect in the territory of the Federal Republic of Germany with the exception of the territory of the former German Democratic Republic.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MR	Mauritania
BE	Belgium	GA	Gabon	MW	Malawi
BF	Burkina Faso	GB	United Kingdom	NL	Netherlands
BG	Bulgaria	HU	Hungary	NO	Norway
BJ	Benin	IT	Italy	RO	Romania
BR	Brazil	JP	Japan	SD	Sudan
CA	Canada	KP	Democratic People's Republic of Korea	SE	Sweden
CF	Central African Republic			SN	Senegal
CG	Congo	KR	Republic of Korea	SU	Soviet Union
CH	Switzerland	LI	Liechtenstein	TD	Chad
CM	Cameroon	LK	Sri Lanka	TG	Togo
DE	Germany, Federal Republic of	LU	Luxembourg	US	United States of America
DK	Denmark	MC	Monaco		

METHOD FOR PRODUCING ECOLOGIC CAPSULE OF NATURAL ORIGIN FOR PRODUCTS WITH CONTROLLED RELEASE OF THE ACTIVE INGREDIENT

The invention relates to a method for producing ecologic capsules of natural origin decomposing in the environment which can preferably be used for selective plant protecting agents with timed release of the active ingredient.

In recent decades all over the world research activity with considerable effort has been performed in order to produce such capsules for applying plant protecting compositions which assure maximal efficiency even in minimal doses, simultaneously prevent leakage of the plant protecting agent from the zone of utilization or unwanted premature decomposition thereof, e.g. upon UV-radiation.

In case, if rooting zone is considered as the zone of utilization, it is of utmost importance that the plant protecting agent should meet here expediently all the harmful organisms, such as fungi and other pathogenic bacteria, weeds or other parasites living in the soil.

The application of the plant protecting agents does not always coincide with the appearance of pathogenic and parasite beings. A further problem lies in the matter of shelf-life of the active ingredients, guaranteed time.

Application of natural polymers or the derivatives thereof forming a complex with the given plant protecting agent belong to successful solutions. The use of e.g. starch or starch derivatives for encapsulating EPTC has also been known, and it has been tried to bind on urea-formaldehyde resin, resulting in the accessory advantage that the carrier serves also as artificial fertilizer.

A further method has been elaborated, by which - starting from emulsion - a solid crust was formed on the surface of drops of colloidal size by means of condensation on phase boundary. This crust assures that the active ingredient gets onto the aimed surface when decomposing or as a semi-permeable film.

Experts are also dealing with the combination of various natural polymers, such as starch, latex and artificial resins. So e.g. shelf-life could successfully be improved, release of the active ingredient could be controlled, when assurance of proper particle size is problematic.

In the Japanese Patent Specifications 0072-806, 2033--103, 2003-795, 0072-804, 1129-138, 8021-602, 0104-095 various cyclodextrin derivatives are used for the formulation of the active ingredients of plant protecting agents.

According to Japanese Patent Specification 8021-605 some porous carriers (e.g. a sponge, paper, a cloth etc.) are impregnated with the volatile plant protecting compositions.

According to the WP Patent Specification 8300-796 for encapsulating of plant protecting agents hollow rods on cellulose basis are used, optionally the outer surface is treated with paraffin.

As it becomes obvious from the WIPO Patent Specification 8303-61 a double capsule system is formed, in which the capsule of larger dimension contains a plurality of microcapsules. For the shaping of the capsule cellulose acetate is used.

According to Japanese Patent Specification No. 8121--212 a gel-type product, i.e. a plant protecting agent is produced from polyacrylate and epoxy-resin for the controlled release of the active ingredient.

In accordance with EP 205 978 carriers containing polyvinyl alcohol and starch are used as capsules for

different pesticides (parathion, trifluraline), feromones and regulators.

In accordance with the EP 121 712 biocides and medicines can be encapsulated by using organophil cellulose ethers.

DE-PS 1 567 066 suggests to encapsulate plant growth regulators and herbicides by using carriers made of thermoplastic synthetic resin and resin soluble in a solvent.

In accordance with the Japanese Patent Specification No. 9 142 264 polysulfone, polycarbonate, cellulose and vinyl-acetate copolymers are applied as carriers for insecticides.

According to US-PS 4 451 635 a carrier is described using water-soluble polymethane-quaternary ammonium salts and ion-exchanging resin.

J 5 7185-344 describes the production of a carrier with timely prolonged release of the active ingredient for attractants, disinfectants and plant protecting agents.

As carrier poly-caprolactame is used, which can be combined with other synthetic materials, so e.g. nitro-cellulose, butylcaoutchouc etc. containing also filler, such as silicagel, calcium carbonate or aluminium oxide.

In accordance with the J5 8010--503 polymer with a high water-absorbing capacity, e.g. inoculated copolymer of starch and polyacrylonitrile is applied for the preparation of agrochemicals, which can optionally be cross-linked.

According to EP - 214 396 A water-soluble polymers are used (e.g. poly-vinyl-alcohol, hydroxy--ethyl-, hydroxypropyl-, methyl-cellulose).

Additionally condensation on the phase boundary is performed by using urea-resin.

EP 158-449 specifies a process for producing capsules for liquids inmsicible with

water, in the course of which a porous crust is formed from the pre-polymerisate of urea-formaldehyde in an organic solvent, to encapsulate plant protecting agents and artificial fertilizers.

According to J6 2201-156 a carrier is made with a slow release of the active ingredient by using binding materials and film-forming materials, as e.g. polyvinyl-alcohol, polyvinyl-acetate, polyethylene and silicon resin.

The US-PS 4 615 883 describes the production of a macrocapsule with a grain size of 0,4 - 5,0 mm, made of hydrogel, which can be produced from sodium-alginate, gelatine and acacia gum.

According to Australian Patent A 8 767-199 a polymer is used, which tends to biological decomposition, in such a manner microorganisms are encapsulated, wherein the number of germs may amount to 10^6-10^{10} unit/g and the size of pearls can be controlled in the range between 0,5 and 40 mm. As material we may use gelatine, alginate, polyacrylamide and cellulose ether.

According to J5 9050-086 a granulate is prepared which is made of some hydrophobic materials, such as paraffin, resin and waxes. Paraffin-shell serves as a coating of grains of artificial fertilizers.

J5 9048-402 offers a solution for preparing capsules for volatile insecticides. Evaporation of the active ingredient is achieved by a controllable calorific process. Calorification is started respectively controlled by diffusing oxygen.

According to the solution, suggested in US-PS 4 400 391 alginate pearls are used for fixing insecticides. As gel-forming agents Cu, Zn, Al, Pb- salts can be applied.

According to research activities in the USA, the results of which were published in 1975 and 1976, starch - - xanthogenate is well suitable for encapsulating plant

protecting agents, as a matrix assuring slow release of the active ingredient. When using xanthogenate cross-linking may be performed by using epychlorohydrine or hydrogen peroxide. In this case water-soluble and insoluble plant protecting agents are encapsulated.

Plant protecting agents having been encapsulated with starch-xanthate are stable, they can be stored without problems. Upon water the active ingredient will be released.

EPTC (S-ethyl-dipropyl-thiocarbamate) and DBPC (1,2--dibromo-3-chloropropane) give a stable capsule, from which volatility of the active ingredient is satisfactory, simultaneously it is well-resistent to sunlight.

Said researchers tested the applicability of latex in respect to the aforementioned active ingredients, while prior to xanthogenation small quantities of latex were added to the starch and cross-linked with sodium-nitrite. In course of some tests zinc sulfate was also used for cross-linking.

In laboratory experiments encapsulation of N--(phosphorous methyl)-glycine and ammonium sulfate could be performed with the best results.

The effect of SBR 1502 (Styrene-butadiene latex) additive on encapsulating DBCP has been tested, at a determined mixing ratio an excellent shelf-time could be achieved.

(Northern Regional Research Laboratory Agricultural Research Service, U.S. Department of Agriculture, Preoria, Illinois 61604) received March 12, 1976).

The aim of our invention:

The capsules as elaborated by us are ecologic, they consist of quickly decomposing and cheap material, the decomposition thereof in the soil takes places without harmful residues. Novelty of the method according to the invention lies in that the aggregate of microcapsule(s) is (are) stiffened in a solid matrix - optionally in colloidal distribution-, in respect to bond strength and releasing

ability it (they) act(s), as if it (they) were individual particles.

We have also recognized another method that is the microcapsule is arranged in the centre of the solid matrix as a result of the process according to the invention and communication with the outer world is realized through the channels and cavities of the matrix.

Another construction is based on the recognition, in so far as the spherical matrix is woven through radially by the polymer threads and funnels of the active carrier, and the microsize appears in one dimension only, while the other size falls into the mezo-range.

The matrix according to the invention can be characterized in that it is insoluble in water but is decomposed in the soil without harmful residues, the active filler does not dissolve in water either and it is ecologic.

A novelty of the method of the invention, lies in that the plant protecting agent intended to be encapsulated are prepared expediently for fixing in the carrier, in the capsule.

E.g. from the well-known active ingredient benomyl a stable suspension is prepared in carbon disulfide, or the heptane solution thereof is used.

Similarly to benomyl, the fungicidally active carbendazim with systemic effect, can be encapsulated. When formulating captan fungicide we started from ethyl alcoholic or acetone solutions.

In accordance with the process according to the invention, when producing microcapsule or capsule we started with natural polymers. E.G. aqueous solution of cellolose, aqueous starch suspension and/or aqueous solution of starch, latex solution, urea-formaldehyde resin of low condensation grade or starting components are used, when condensation is carried out in course of capsulation, in the presence of a coagulation catalyst.

In the initial phase of capsule production optionally active carbon of well-defined grain size can be added to the polymer compound being present. In the course of the capsule--forming process, taking place in the mixture of mineral and organic acids, surfactants are used, as e.g. BEROL products and as a cross-linking agent copper complexes are used. In certain cases as filler polyacrylonitrile in a pulverized form is used of a grain size of 1 to 10 micron.

The formulation of the capsules may be carried out by methods known per se, however different methods of drying can also be used.

The active ingredient (solution, suspension, emulsion) is absorbed by the finished capsule by methods known per se. In certain cases, by using the method according to the invention, condensation on the phase frontier may be carried out too.

The details of the invention are illustrated in the following examples.

Example 1

A carrier (capsule) for encapsulating selective herbicides can be prepared, as follows:

100 dm^3 cellulose solution is weighed into a tank of 0.25 m^3 equipped with an agitator (related to the cellulose a 5% solution), 50 dm^3 starch suspension are admixed thereto (suspension may be prepared from corn starch in a 5% NaOH solution, while the suspension content of the solution amounts to 10%), 1 dm^3 ammonia latex solution with an active ingredient content of 60% is added too.

After vigorous stirring 10 dm^3 urea-formaldehyde-resin precondensate are admixed, while the required catalyst is added to the acidic solution to precipitate.

As a cross-linking agent we add 1 dm^3 of 1% copper - tetramine hydroxyde. The polymer mixture thus produced is put into the acidic bath in the shaping equipment known

per se, which is preferably an aqueous mixture of 10% sulfuric acid and 5% acetic acid. The bath contains in a concentration of 1-2 g/dm^3 a surfactant (BEROL SPINN 62).

The capsule thus obtained is washed and dried. We obtain a granular carrier of a diameter of 1-2 mm, thereafter the prepared plant protecting agent is adsorbed thereon.

The application of the product into the soil is carried out by methods known per se in the period of sowing of cultivated plants. Upon the effect of soil moisture caused by rainwater the active ingredient will be released gradually.

Example 2

A cellulose solution - of a concentration of 4,8 - - 5,3% related to cellulose - is added into a 0,25 m^3 enamelled tank equipped with an agitator. The cellulose solution contains 80% cellulose xanthogenate, 15% carboxy--methyl cellulose, as well as 5% starch-xanthogenate.

6 kg finely-divided active charcoal are added to the aforementioned solution with an active surface of 1000 m^2/g, furtheron finely-ground bran in an amount of 20 kg. Finally 2 kg of urea-formaldehyde pre-condensate are added, thereafter the mixture is stirred for two hours with an Anker-agitator. The solution thus obtained is allowed to pass through a sieve cloth of 100 /um mesh.

The filtered polymer concentrate is converted into drops. Upon contacting them with acid fume drops are coagulated, the coagulated substance is washed and dried. We thus obtain a carrier of a grain-size of 0.5 - 1.0 mm, by the aid of which herbicide with a selective effect (e.g. EPTC) is encapsulated by a method known per se.

The used polymer components bind the plant protecting agents with different strength, thus the combined carrier guarantees timely programmed release of the active ingredient.

The release of the active ingredient is completed with the complete decomposition of the carrier in the soil.

Example 3

Using the equipment as described in example 2, we admix 10 kg of pulverized acrylonitrile - styrene sulfonate copolymer to 200 dm^3 cellulose solution, (grain size in the range between 1 and 10 micron). Due to the ion-exchanging groups of said additive the binding of the plant protecting agent and the controlled release of the active ingredient can be achieved.

Claims

1. A process for producing capsule or microcapsule containing cellulose and/or starch, characterized in that 0-50 % by weight of polymers are added to the capsule material of natural origin at a temperature of 10 to 50 C^{o}, the suspension is vigorously stirred, thereafter 0 to 50 % by weight of urea-formaldehyde resin pre-condensate are admixed, the colloidal solution thus obtained is applied onto the acid solution mixture - preferably 10 % by weight of sulphuric acid - containing 0,1 to 5 % by weight of cross-linking catalyst, preferably ammonium sulfate, furtheron 0,01 to 5 % by weight of ethoxylated amine surfactant, the capsules thus obtained are washed and dried at 40 to 100 C^{o}, thereafter various active ingredients respectively the solutions thereof are contacted with the capsule, and the absorbed capsule is powdered.

2. A process as claimed in claim 1, characterized in that in order to produce capsules as gel-forming additives ammonium sulfate, ammonium carbonate, zinc tetramine hydroxyde or copper tetramine hydroxyde are added.

3. A process as claimed in claim 1, characterized in that in addition to the micro-capsule structure fixed in the matrix, by using the so-called powdering method, by the additional application of a mixture made of the fine grist of one or more components onto the grain surface a loosely bond crust is produced resulting in a double shell-structure, while adhesion is achieved by a natural polymer solution or the powder thereof, preferably pulverized potassium humate or solution, or pulverized carboxy-methyl cellulose or solution.

4. A process as claimed in claim 1 and 3, characterized in that when preparing the active ingredient, particularly a plant protecting agent to be

encapsulated, a stable suspension or emulsion is prepared of a solvent being efficient and unharmful from the point of view of ecology, as well as of additives (e.g. carbon disulfide) promoting adsorption in the capsule and improving chemical bond, while in the soil proper desorption is assured upon the effect of moisture.

INTERNATIONAL SEARCH REPORT

International Application No PCT/HU 90/00021

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC[5]: B 01 J 13/14, A 01 N 25/28

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
Int.Cl.[5]	B 01 J 13/02, B 01 J 13/14, A 01 N 25/26, A 01 N 25/28

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category [10]	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
A	EP, A, 0 305 212 (ROHM AND HASS) 01 March 1989 (01.03.89), see examples; claims.	(1-4)
A	EP, A, 0 205 978 (PENNWALT CORP.) 30 December 1986 (30.12.86), see examples; claims.	(1-4)
A	EP, A, 0 041 210 (HOECHST AG) 09 December 1981 (09.12.81), see examples; claims.	(1-4)

---

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
07 June 1990 (07.06.90)	20 June 1990 (20.06.90)
International Searching Authority	**Signature of Authorized Officer**
AUSTRIAN PATENT OFFICE	

Form PCT/ISA/210 (second sheet) (January 1985)

Anhang zum internationalen Recherchenbericht über die internationale Patentanmeldung Nr.

Annex to the International Search Report on International Patent Application No. PCT/HU 90/00021

Annexe au rapport de recherche internationale relatif à la demande de brevet international n°.

In diesem Anhang sind die Mitglieder der Patentfamilien der im obengenannten internationalen Recherchenbericht angeführten Patentdokumente angegeben. Diese Angaben dienen nur zur Unterrichtung und erfolgen ohne Gewähr.

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned International search report. The Austrian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

La présente annexe indique les membres de la famille de brevets relatifs aux documents de brevets cités dans le rapport de recherche internationale visé ci-dessus. Les renseignements fournis sont donnés à titre indicatif et n'engagent pas la responsabilité de l'Office autrichien des brevets.

Im Recherchenbericht angeführtes Patentdokument Patent document cited in search report Document de brevet cité dans le rapport de recherche	Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
EP-A - 305212		AU-A1-21175/88	20-04-89
		BR-A - 8804294	14-03-89
		CN-A - 1032118	05-04-89
		DK-AO- 4755/88	25-08-88
		DK-A - 4755/88	27-02-89
		EP-A1- 305212	01-03-89
		FI-AO- 883926	25-08-88
		FI-A - 883926	27-02-89
		IL-AO- 87560	31-01-89
		JP-A2- 1070505	16-03-89
		NO-AO- 883742	22-08-88
		NO-A - 883742	27-02-89
		PT-A - 88341	01-09-88
		ZA-A - 8806080	26-04-89
EP-A - 205978		AT-E - 52405	15-05-90
		BR-A - 8602466	17-03-87
		CA-A1- 1252712	18-04-89
		EP-A1- 205978	30-12-86
		EP-B1- 205978	09-05-90
		ES-A1- 555450	01-07-87
		ES-A5- 555450	31-07-87
		ES-A1- 8707079	01-10-87
		HU-A2- 41949	29-06-87
		IL-AO- 78859	30-09-86
		IL-A1- 78859	15-08-89
		IN-A - 164999	22-07-89
		JP-A2-62023435	31-01-87
		PH-A - 21802	29-02-88
		US-A - 4657582	14-04-87
		ZA-A - 8604004	29-04-87

Anhang zum internationalen Recherchenbericht über die internationale Patentanmeldung Nr.

Annex to the International Search Report on International Patent Application No. PCT/HU 90/00021

Annexe au rapport de recherche internationale relatif à la demande de brevet international n°.

In diesem Anhang sind die Mitglieder der Patentfamilien der im obengenannten internationalen Recherchenbericht angeführten Patentdokumente angegeben. Diese Angaben dienen nur zur Unterrichtung und erfolgen ohne Gewähr.

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned International search report. The Austrian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

La présente annexe indique les membres de la famille de brevets relatifs aux documents de brevets cités dans le rapport de recherche internationale visé ci-dessus. Les renseignements fournis sont donnés à titre indicatif et n'engagent pas la responsabilité de l'Office autrichien des brevets.

Im Recherchenbericht angeführtes Patentdokument Patent document cited in search report Document de brevet cité dans le rapport de recherche	Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
EP-A - 41210		AR-A1- 229837	30-12-83
		AT-E - 11144	15-01-85
		AU-A1-71163/81	10-12-81
		AU-B2- 540890	06-12-84
		BR-A - 8103370	16-02-82
		CA-A1- 1180608	08-01-85
		DD- C- 159147	23-02-83
		DE-A1- 3020781	10-12-81
		DE-C2- 3020781	18-11-82
		DE-C0- 3168118	21-02-85
		EP-A1- 41210	09-12-81
		EP-B1- 41210	09-01-85
		ES-A1- 502509	01-04-82
		ES-A5- 502509	16-04-82
		ES-A1- 8203233	01-07-82
		IL-A0- 62994	31-07-81
		IL-A1- 62994	31-12-84
		JP-A2-57021932	04-02-82
		NZ-A - 197236	12-04-83
		PH-A - 17491	04-09-84
		PT-A - 73107	01-06-81
		PT-B - 73107	21-10-82
		TR-A - 21304	01-03-84
		US-A - 4409201	11-10-83
		ZA-A - 8103611	30-06-82